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WADC TECHNICAL REPORT 54-466

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PRODUCTION OF LEATHERS RESISTANT TO POWERFUL OXIDANTS AND REDUCTANTS

NICHOLAS D. CHERONIS
MERILYN A. WENTE

THE SYNTHETICAL LABORATORIES

JUNE 1955

WRIGHT AIR DEVELOPMENT CENTER

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MATERIALS LABORATORY
CONTRACT No. AF 33(600)-23872
PROJECT No. 7320

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
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FOREWORD

This report was prepared by The Synthetical Laboratories, Chicago, Illinois under USAF Contract No. AF 33(600)-23872. This contract was initiated under Project No. 7320, "Air Force Textile Materials", Task No. 73200, "Functional Air Force Textiles, Leather and Paper Materials", formerly RDO No. 612-13, "Textile Materials for Air Force Clothing", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. H. H. Brandt and Lt R. Lichtman acting as project engineers.

This report covers period of work conducted from 11 April 1953 to 15 May 1954.

ABSTRACT

Various methods of rendering leathers resistant to the powerful oxidants and reductants employed as fuels in guided missiles were investigated. It was found that once these chemical agents penetrate within the interstices of leather, it is impossible to obtain protection by covering the fiber bundles with materials resistant to the action of oxidants and reductants.

A two-step method was developed for the production of experimental leathers resistant to the action of fuming nitric acid which was selected as the most powerful corrosive agent of the fuels employed. In the first the leather is chrometanned and then treated by the emulsion method (developed under a seven year contract from the Quartermaster's Office, U. S. Army) whereby 10 to 15% of a "filler" polymer is deposited within the interstices of the hide. This serves to close most of the free spaces in the outer subsurface layers and also as an anchorage of the acid resistant film. In the second step, a resistant polymeric film of about 5 to 6 mils thickness is deposited. From the number of polymers investigated for acid-resistance, a few were found which give excellent acid-resistance. As it was to be expected, films resistant to fuming nitric acid exhibit resistance to 90% hydrogen peroxide which is also a powerful oxidant. Experimental leathers having good physical characteristics and excellent acid-resistance were prepared.

An additional method of evaluation of the experimental leathers was employed besides those used for this type of work. It consists of making stained microsections of the leathers before and after exposure and obtaining evidence of corrosion and resistance by photographic methods.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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We wish to acknowledge the excellent cooperation and help on the work of this project from the following companies and individuals:

The J. Greenebaum Tanning Company of Chicago and Milwaukee for furnishing most of the leathers used in this project and for the use of the facilities of the South Milwaukee plant for the tannery scale production of the experimental leathers;

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President Harry Gideonse of Brooklyn College for cooperation given us by the Department of Chemistry in allowing space to be used for the early development of this work and later for some of the theoretical aspects of the problem.

SECTION I

SCOPE OF THE INVESTIGATION

A. GENERAL NATURE OF THE PROBLEM

The present report is a summary of the investigation carried under Contract No. AF 33(600)-23872 from 11 April 1953 to 15 May 1954 on the development of leathers resistant to powerful oxidants and reductants employed in the propulsion of guided missiles. The general scope of the investigation was to deposit materials within and on the outer surface of leathers so as to offer protection to personnel handling various "missile fuels" without affecting their most desirable characteristics.

The problem of obtaining protection against powerful oxidants is of general interest to both the Armed Forces and chemical industries. The use of fuming nitric acid, 90% hydrogen peroxide and hydrazine hydrate in guided missiles has made it necessary to obtain protection against these materials. The materials which are expected to offer resistance are such perfluoro compounds as Teflon and Kel-F. However, such resistance to powerful chemicals is exhibited only when the film is continuous. The application of Teflon and Kel-F films to such a fibrous material as leather presents two insurmountable difficulties. The first is that application requires high temperatures and the leather is seriously damaged; the second is that such a film does not possess the required flexibility.

It appeared therefore that a systematic search had to be made in order either to find commercially available materials or to develop new ones which when deposited on the leather would give a product which, while suitable for the construction of gloves and shoes, would still be resistant to the powerful chemicals and have satisfactory wear resistance and flexibility.

B. SPECIFIC OBJECTIVES OF THE INVESTIGATION

The specific objectives of the investigation as set forth in the contract are: "...the development of leather to be used in protective handwear and footwear for personnel handling various fuels and oxidants employed in rocket propulsion. The leather shall have good flexibility between -25°F and 110°F, good abrasion resistance, tensile strength, bursting strength and aging characteristics. In addition the leather on prolonged and intimate contact with the skin shall not cause dermatitis." More specifically the leather should exhibit appreciable resistance to the oxidants and reductants listed in Table 1.

TABLE 1

OXIDANTS AND REDUCTANTS FOR WHICH PROTECTION IS DESIRED

1. White fuming nitric-acid (HNO_3, 97.5% Min.)
2. Mixed acids (fuming sulfuric and white fuming nitric)
3. Hydrogen peroxide (90%)
4. Furfural alcohol
5. Ethyl alcohol
6. Aniline
7. Hydrazine (94%)
8. Anhydrous ammonia
9. Ammonia (commercial)
10. Liquid oxygen

C. DESIRABLE CHARACTERISTICS OF EXPERIMENTAL LEATHERS TO BE DEVELOPED

1. PHYSICAL CHARACTERISTICS WHICH MUST BE RETAINED

The physical characteristics of leathers which are of importance in the construction of military glovewear and footwear are summarized in Table 2.

TABLE 2

DESIRABLE PHYSICAL CHARACTERISTICS OF MILITARY LEATHERS

Physical Characteristics	Measurement
Wear resistance	Abrasion resistance and wear tests
Elongation	Specs /a/ and A.L.C.A. /b/
Tensile strength	" " "
Stitch tear	" " "
Water repellency	Dynamic and performance
Water vapor permeability	A.L.C.A. method
Low temperature flexibility	Specs. A.L.C.A.
Resistance to aging	" "
Gloviness	Subjective by tanners
Feel	" " "
Appearance	" " "

/a/ Specs: Various specifications as set forth by the military agencies;
/b/ A.L.C.A.: Method of American Leather Chemists Association

Inspection of the desirable qualities of military leathers suggests that in attempting to introduce other materials into them so as to impart resistance to the action of powerful oxidants one or more of these properties may have to be modified or even entirely sacrificed.

2. PHYSICAL CHARACTERISTICS OF LEATHER WHICH CAN BE SACRIFICED

In general the deposition of polymers within the interstices of leathers enhances most of the desirable properties except water vapor permeability or the breathing qualities of leathers. In a previous investigation on military leathers carried in this laboratory for the office of the Quartermaster General the author showed that it is possible to obtain oriented deposition of polymers within the interstices of leathers without affecting appreciably the water vapor permeability. It seemed at the outset of the present investigation that the water vapor permeability of leather might have to be entirely sacrificed in order to obtain adequate resistance to such powerful oxidants as fuming nitric acid. This consideration was based upon the following known facts:

(a) Leather contains a large amount of empty spaces between the fiber bundles of collagen.

(b) The empty spaces in a particular sample of leather depend on the area of the hide from which the sample is taken. Generally the areas of high fiber density (along the backbone) have 30 to 40% empty space and those of low fiber density (breast and belly) have 50 to 60%.

(c) The passage of any liquid through a piece of leather (from one side to the other) first wets the contact surface then fills the interfiber empty spaces and channels toward the opposite side of the contact side. During such a passage the liquid wets the interfiber bundles and individual fibers.

From these considerations it appears unlikely that a material could be developed which when introduced within the interstices of leather could completely cover every fiber and fiber bundle so as to offer protection against fuming nitric acid. Further, even assuming that such a development was possible then it would be necessary to fill the empty spaces completely in order to stop the channeling of the acid from one side to the other. It appeared very unlikely that any appreciable water vapor permeability could be retained under these conditions. Therefore, it was decided before work on the project was initiated that if it was found necessary the comfort factor due to the breathing qualities of leather had to be sacrificed.

From previous experience on the deposition of all kinds of materials within the interstices and on the surface of leathers it was expected that none of the other physical properties of leather listed in Table 2 would have to be profoundly changed.

3. CHARACTERISTICS TO BE IMPARTED BY DEPOSITION OF MATERIALS ON LEATHERS

The characteristics to be imparted to the leathers are as follows:

(a) Resistivity to the oxidants and reductants listed in Table 1. Of these the most important are: fuming nitric acid (97.5% Min), and hydrogen peroxide (90%).

(b) Fair to good flexibility between -25°F and 110°F.

(c) Best obtainable abrasion resistance.

(d) Best obtainable tensile and bursting strength.

(e) Good aging characteristics.

(f) Lack of irritation to skin.

SECTION II

SELECTION OF EXPERIMENTAL METHODS

A. THEORETICAL CONSIDERATIONS

The exploratory phase of the work consisted in dividing the approach to the problem into three areas, then considering within each area those steps which on the basis of theory and prior knowledge would most likely lead to the desired results. The three areas are: (1) selection of materials which are likely to offer resistance to fuming nitric acid; (2) deposition of the materials on the leathers; (3) evaluation of the resultant experimental leathers.

1. MATERIALS WITH APPRECIABLE RESISTANCE TO FUMING NITRIC ACID

Fuming nitric acid (97.5% Min.) was selected as the chemical agent (of those listed in Table 1) with which to measure resistance of the experimental leather developed. It was assumed with considerable certainty that if a treated sample exhibited an appreciable resistance to fuming nitric acid it would also be resistant to all other chemical agents listed in Table 1.

The groups of materials which were selected on the basis of theory to be tried for resistance to fuming nitric acid are listed in Table 3.

TABLE 3

MATERIALS SELECTED FOR RESISTANCE TO FUMING NITRIC ACID

1. Perfluoro compounds
2. Fluoro and perfluoro polymers
3. Silicon polymers
4. Perfluorosilicones
5. Polythene polymers
6. Polybutene polymers
7. Polyisobutene polymers
8. Chloroprene polymers
9. Thiokol polymers
10. Fine inorganic (colloidal) materials: silicates, sulfides, graphites, etc.

The discussion of the various groups of materials is given in Section III, Pages 8-11. Suffice it to state that by exploratory work most of these groups were investigated and a number were selected which proved to have appreciable acid-resistance.

2. DEPOSITION OF MATERIALS IN LEATHERS

It was decided to investigate the introduction of the acid resistant materials into the leather both by the "solvent" and "emulsion" method. The former consists in dissolving the material in an organic solvent, impregnating the leather in the solution and then evaporating the solvent. The latter consists in emulsifying the material in a water phase and then tumbling the wet leather in a mill with the emulsion whereby the emulsified particles are discharged and deposited within the interstices of the leather.

In order to obtain a uniform deposition of materials having high molecular weight, it appeared that the emulsion method was most likely to succeed. For example, deposition of 10% (on a dry weight basis) of a rubber in a sample leather by the solution method leads to a product with undesirable physical characteristics due to surface or subsurface deposition. On the other hand, deposition of 15% of the same rubber can be made by the emulsion method with no surface deposition.

3. EVALUATION METHODS

Two methods were suggested by the Technical Staff of the Wright Air Development Center. The "screening test" consists of placing a disc of leather in contact with fuming nitric acid on one side and determining the effect of 30-minute exposure. The "permeability test" was employed on leathers which exhibited considerable resistance in the screening tests; it involved the measurement of the rate of passage of fuming nitric acid through a treated sample. Both tests are described in Section V.

An additional evaluation procedure was developed during the progress of this work. The procedure (microscopical test) involves the preparation of stained microsections of sample leathers which were exposed to fuming nitric acid and the examination of these under a microscope. This method reveals in great detail the structural changes on the surface and fiber bundles produced by the acid or other chemical agents.

B. EFFECT OF FUMING NITRIC ACID ON UNTREATED LEATHERS

In order to obtain a "base line" for comparison about 100 samples from "heavy duty" and "regular" Army Specifications glove leathers were exposed to the action of fuming nitric acid for 30 minutes; the samples were washed with water, then neutralized to pH 8.2 (with sodium bicarbonate), then examined for evidence of gross changes. The samples were allowed to dry for 24 hours and again examined. To summarize the results of this investigation:

(a) Untreated leathers are profoundly affected by even 10 minute exposure to fuming nitric acid. If the acid is applied on the grain side and a deformation is present which permits rapid passage of the acid within the interstices a violent reaction may start with extensive carbonization.

(b) All samples of untreated leather after 30 minutes' exposure show attack leading to the destruction of 20 to 40% of the surface and ultimate hardening and cracking even after neutralization.

(c) The penetration and attack by the acid is more rapid on areas of low fiber density than on areas of high fiber density and greater if the leather is bent or distorted as in flexing than when the leather lies flat.

SECTION III

SELECTION OF MATERIALS HAVING RESISTIVITY TO FUMING NITRIC ACID

A. INTRODUCTION

The groups of materials which were selected for exploratory experimentation for resistance to fuming nitric acid were listed in Table 3, Page 5. Representative members from most groups were selected and incorporated within and on the surface of leathers which were then evaluated. In a few cases of polymers films of 2 to 6 mil thickness were cast and tried for acid permeability (Section V). However, it was felt that even if a material gave a promising acid-resistance alone, it could not be assumed that it would exhibit the same resistance when applied either as a film or as a filler in leather. In the following sections a brief discussion is given of each group of materials which were tried, together with a summary of the results obtained.

B. PERFLUORO COMPOUNDS AND POLYMERS

Table 4 lists the perfluoro compounds and polymers which were tried on leathers. The perfluoro amide and ethanol-amides were prepared from the corresponding carboxylic acids. The perfluorooctanoic and decanoic acids were obtained from commercial sources. The perfluoroglutaric acid was prepared by oxidation of 1, 2-dichlorohexafluorocyclohexene. The use of the amides was made with the idea of obtaining a better bond between the perfluoro compound and the proteins of the leather fibers, than the bond obtained with the perfluoro oils, greases and waxes.

The results summarized in Table 4 indicate that perfluoro compounds introduced into the interstices of leather improve its resistance to attack by fuming nitric acid but fail to give the desired protection. This is not due to attack by the acid on the perfluoro compounds but rather to the discontinuity of the perfluoro film, which permits direct contact between the acid and the leather fibers.

The preparation of perfluoro polyamides (nylon type) by reaction of a perfluoro dicarboxylic acid such as perfluoroglutaric acid and a perfluorodiamine such as 1, 6-diaminoperfluorohexane was considered but very little work was done in this direction. The preparation of such polymers is involved and costly; moreover, other readily available polymers offered good protection.

C. SILICONE POLYMERS

Table 5 lists the Silicone polymers which were deposited in leathers and evaluated for resistivity to fuming nitric acid.

TABLE 4

PERFLUORO COMPOUNDS AND POLYMERS APPLIED ON LEATHERS TO IMPART RESISTANCE TO FUMING NITRIC ACID

Perfluoro Compound or Polymer	Method of Application on Leather	Depn. %	Resistivity to Fuming HNO_3 as Measured by Acid-Cup Method
Perfluoro octanoic acid amide /a/	Solvent /d/	25	Poor protection /f/
Perfluoro octanoic acid ethanolamide /a/	"	25	" "
Perfluoro decanoic acid ethanolamide /a/	"	25	" "
Perfluoro glutaric acid diamide /a/	"	21	" "
Kel-F oil polymer #1 /b/	"	27	" "
Kel-F oil polymer #3 /b/	"	30	" "
Kel-F oil polymer #10 /b/	"	30	" "
Kel-F grease polymer #40 /b/	"	32	" "
Kel-F wax polymer #150 /b/	"	25	" "
Kel-F mixture 3, 10 & 40	"	19	" "
Kel-F Polymer #NW-25 with oil #10 /c/	Emulsion /e/		Better protection than any perfluoro compound or polymer /g/

/a/ Prepared at The Synthetical Laboratories; /b/ purchased from M. W. Kellogg Co.; /c/ M. W. Kellogg Co. (the polymer in a toluene dispersion); /d/ the compound was dissolved in benzene-hexane mixture and the leather impregnated, then the solvent evaporated; /e/ the polymer was diluted with toluene and then emulsified and deposited in leather as described in Section IV of this report; /f/ poor resistance indicates that though the treated leather has a greater resistance than untreated leather, on standing becomes hard and cracks; /g/ the leather on standing becomes hard.

TABLE 5

SILICONE POLYMERS DEPOSITED IN LEATHERS TO IMPART RESISTIVITY TO FUMING NITRIC ACID

Silicone Polymer	Method of Application	Depn. %	Resistivity to Fuming HNO_3 as Measured by Acid-Cup Method
Methyl polysiloxanes /a/	Emulsion /c/	20	Poor protection
Ethyl polysiloxanes /b/	"	20	" "
Amyl polysiloxanes /b/	"	20	" "
Nonyl polysiloxanes /b/	"	20	" "
Ethyl polysilazanes /b/	Solvent	10	" "
Mixture of ethyl & amyl polysiloxanes with surface coating of ethyl polysilazanes /b/	Emulsion & Solvent	21	Fair to good /d/

/a/ Dow Corning Corporation, DC 200, 12,500 cstks;/b/ prepared by the Synthetical Laboratories; /c/ method described in Section IV of this report; /d/ the leather was not attacked, however the surface coating of the aminosilane peeled off.

The results summarized in Table 5 clearly indicate that in order to impart acid-resistance to leather it is necessary to place a "blocking film" on its surface and avoid any passage of the acid within its interstices.

D. POLYDIENE AND POLYSULFIDE POLYMERS

Under this group are included the polythenes, the synthetic rubbers (of various types such as GR-S, Neoprene, Butyl, and the like) and the polysulfide rubbers known as Thiokols. All of these polymers were obtained from commercial sources. Table 6 lists the various types of polymers of this group which were employed either for deposition within the interstices or as an acid resistant film on the surface of leather. It will be noted that the evaluation of treated samples is not given since no polymer was used by itself but rather in a combination treatment described in subsequent sections.

TABLE 6

POLYDIENE AND POLYSULFIDE POLYMERS USED IN LEATHER TREATMENTS TO IMPART RESISTIVITY TO FUMING NITRIC ACID /a/

Polymer	Chemical Nature	Source
Alathon 1	Polyethene	E. I. DuPont de Nemours Co.
Alathon 7	"	"
Alathon 8	"	"
Neoprene rubber	Polychloroprene	Enjay Corporation
Butyl rubber	Polyisobutene	" "
Vistanex LM	"	" "
Vistanex MS	"	" "
Vistanex B80	"	" "
Thiokol LP-2	Polyfunctional mercaptan	Thiokol Chemical Corporation

/a/ The detailed description of the leather treatments with these polymers with the evaluation of the experimental leathers appears in the subsequent section.

SECTION IV

DEPOSITION OF POLYMERS IN LEATHERS TO IMPART ACID RESISTIVITY

A. THE TWO-STEP METHOD FOR PRODUCING ACID RESISTANT LEATHERS

The method as finally developed fits into standard leather manufacturing procedures. In the first step the leather is chrometanned, then neutralized to about pH 3.5 to 4.2, then washed free of electrolytes without fat-liquoring or stuffing. The tanned wet hides are then preconditioned to deposition of polymers by the emulsion method, then "crusted" for 24 to 48 hours. The leathers are then treated in a standard mill with the emulsion of a polymer (listed in Table 6) so that a deposition of 10 to 20% on the dry weight of leather is obtained. The leather is then dried, cured and staked. By this treatment most of the empty spaces (on the outer areas of grain and flesh) are filled with a nonmigrating and firmly attached polymeric film in contradistinction to the mobile fats and oils which are employed to fill the commercially available leathers. This completes the first step.

In the second step the leathers are slightly buffed on the grain side and are then coated with a flexible adhering film of a polymer (listed in Table 6). This film accounts for most of the acid resistance. The details of the treatment and the techniques employed are described in the present and following sections.

B. TYPES OF LEATHERS USED

Table 7 lists the types of leathers used for the production of experimental leathers.

TABLE 7

TYPES OF HIDES USED FOR THE PRODUCTION OF ACID RESISTANT EXPERIMENTAL LEATHERS

Type of Hide	Oz. Thickness	Tannage	Source
Cowsides	3	Chrome	J. Greenebaum Tanning Co., Milwaukee, Wis.
Horsesides	3	"	" "
Cowsides	3	"	Horween Leather Co., Chicago, Ill.
Horsesides	3	"	" "
Cowside splits	2.5	"	Lichtman Tanning Corp., Newark, N. J.
Steerhide splits (upper)	4-4.5	"	" "
Cowsides	2	"	J. Greenebaum Tanning Co., Milwaukee, Wis
Cowsides	3	Politan	John R. Evans, Camden, N. J.

It will be noted that most of the leathers produced are for glovewear. For one thing, the thickness of glovewear leathers is not as large as that of upper leathers and hence the deposition is easier; furthermore, any method developed for glove leathers can be applied with some modification to upper or other types of leathers.

The emulsion method gave better deposition on chrometanned leathers than on those which were vegetable tanned, therefore chrometanning was employed. Politan-tanned leather was used only once in order to determine whether the method was applicable to other than chrometanned leathers.

C. THE EMULSION METHOD FOR DEPOSITION OF POLYMERS INTO THE INTERSTICES OF LEATHERS

1. INTRODUCTION

The method was developed in this laboratory under a series of contracts from the Quartermaster General's Office between 1945 and 1952. The complete description of the method appears in the Research and Development Report Footwear and Leather Series No. 8, "The Development of Water Resistant Leathers," April 1954, pp. 24-155.

It should be noted that the completion of the present project in a short period of time and at a very low cost would not have been possible if it had not been based on work which already had been done by another branch of the Defense Department.

The various steps of the emulsion method for deposition of polymers into the interstices of leathers are briefly discussed.

2. PRECONDITIONING FOR EMULSION TREATMENT

The process begins immediately after the hide has been tanned. It is first neutralized by standard tannery procedures to a pH between 3.8 and 4.2 and washed completely free of electrolytes. Ten grams of the washed leather are cut into small pieces and suspended for 24 hours in 100 ml of distilled water. About 10 to 20 ml of the filtrate are used for the pH determination and exactly 50 ml are evaporated and dried at 105°C to constant weight for total solids. The dish is ignited and the ash is used for determination of metallic ions. The ions present should be within 50 to 100 mg per 100 grams of dry leather for optimum operation.

The tanned hide with adjusted pH and free of electrolytes is now tumbled in a standard mill with an emulsion of preconditioner so as to deposit between 5 and 10% of it within the leather. The preconditioner is deposited so as to avoid rapid exhaustion of the polymer emulsion and to prevent the deposition of the polymer on the surface of the leather. The basis for the selection of the preconditioner is the following: the charge of the emulsified polymeric particle is determined to a very large extent by the emulsifier or system of emulsifiers employed. Therefore, the deposition of a fatty mixture containing compounds related to the emulsifiers gives successful mill operation.

Generally, for glove leathers 8 to 10 % of the preconditioning mixture is deposited, while for upper leathers 5 to 6 % is sufficient.

After the deposition of the preconditioner the leather is dried and "crusted" for 48 hours. Since the preconditioner mixture contains some fatty material it is possible to rewet the leather by standard tumbling methods.

3. EMULSIONS FOR DEPOSITION OF POLYMERS WITHIN THE INTERSTICES OF LEATHERS

This topic is covered in great detail on pages 140-175 of the Quartermaster Footwear and Leather Series No. 8, and therefore only a brief discussion is given in the present report.

Generally there are two types of emulsions for leather treatment:

(a) Emulsions prepared from monomers by emulsion polymerization methods with selected systems of emulsifiers. The resulting lattices are suitable for leather deposition. Examples of this are the synthetic rubber lattices of the GR-S type having an acid pH described on page 46 of the QM report. This type was not used in the present problem.

(b) Emulsions prepared from low molecular intermediate polymers without extensive cross-linkages. This type of emulsion was used throughout the work reported.

The preparation of the emulsion begins with dispersing the polymer into an appropriate solvent. The ratio of solvent and polymer is such that in the final "stock emulsion" the polymer content is between 10 and 20% by weight and the solvent between 20 and 30%. Generally the higher the molecular weight the lower the content of polymer. Thus in a series of three polybutene polymers having molecular weights of 4,000, 20,000 and 75,000 the content of polymer in the final stock emulsion is 20%, 10% and 5% respectively.

To the dispersion of polymer is added the proper amount of plasticizer. The selection and effect of plasticizer is discussed in a subsequent section. Generally for glove leathers the plasticizer content varies between 15 and 30% of the weight of the polymer.

The polymer-plasticizer dispersion is mixed with the appropriate amount of water containing the emulsifying system and then passed once or twice through a colloid mill having 8,000 to 12,000 rpm. This gives the stock solution.

The following Formula A is an example of a recipe for a stock emulsion used in the present project:

Formula A

Thiokol LP-2	87.5	grams
Vistanex-MS	158.5	"
Indopol (Polybutene)	54.0	"
Xylene	1070.0	"
Toluene	356.5	"
Emulsifier (Mixed, Anionic nonionic, #350)	21.0	"
Masking Odor	2.0	"
Water	1250.5	"
Total	3000.0	grams
Percent of solids	10.0	
pH	8.0	

This type of emulsion is stable for several months and is diluted prior to introduction in the mill. The emulsifying system is discussed further on in this section.

4. MILL OPERATION

The preconditioned leather is wetted by tumbling at 55 to 60°C according to standard tannery procedures. The tumbling should be sufficient to completely wet and loosen the fiber bundles. Usually 30 to 45 minutes of tumbling is sufficient if the leather has been in water for 24 hours. The water is drained and the emulsion is diluted with hot water so as to have a content of solids about 3 to 4%. The amount of emulsion used depends on the level of deposition which for glove chrometanned leathers can be 5 to 40% on a dry weight basis. The hot diluted emulsion is placed in the mill with the leather and a sample is taken for "solids" and "pH" measurements. The mill is then closed and the leather tumbled for 60 to 90 minutes.

within the interstices in conjunction with another polymer always increases the bonding of the acid-resistant surface film. This is due apparently to the presence of -S- and -O- linkages in the Thiokol polymer.

When there is no bonding between the polymer within the interstices and the acid-resistant film the latter tends to peel off readily and further leads to poor acid resistance.

2. PLASTICIZERS AND EMULSIFIERS

Table 8 lists the plasticizers and types of emulsifying systems used in this work.

TABLE 8

PLASTICIZERS AND EMULSIFYING SYSTEM EMPLOYED FOR LEATHER TREATMENTS

Plasticizers /a/	Emulsifying Systems /b/
Indopol-Polybutene-IP	Mixed Anionic-nonionic #160
Dioctylphthalate DOP	Anionix mixture #200
Dibutylphthalate DBP	Nonionic mixture #250
Tricresyl phosphate TCP	Cationic mixture #260
Kel-F oils /c/ Kel-F	Mixed-anionic-nonionic #350

/a/ The underlined initials are employed in subsequent tables;
/b/ the numbers of the emulsifying system are employed in subsequent tables;
/c/ Kel-F oil #10 and 40.

The influence of the nature and amount of plasticizer is shown by comparing runs #230, 231, 233 and 245 in Tables 9 to 12 which follow. It appears that one of the important factors in determining physical characteristics of feel, appearance and gloviness is the extent to which the polymer is plasticized. Generally good physical characteristics are obtained with a ratio of polymer to plasticizer 7:3 to 7.5:2.5.

3. LEVEL OF DEPOSITION

Various levels of deposition were tried from 10 to 35%. It appears from the overall considerations that the deposition should not fall appreciably below 10% and not be higher than 20% based on the dry weight of the leather. A high deposition level leads to stiffness, a very low deposition level leads to poor adherence of the acid-resistant film.

4. DEPOSITION PATTERN

The distribution of the polymer within the leather interstices or deposition pattern is determined by preparation of micro sections from the treated leathers. These are first bleached with hydrogen peroxide, then stained (see QM Report pp. 196-207) and examined under the microscope. The distribution of polymer mostly in the subsurface layers and very little in the middle leads to stiffness.

The microscopical examination was developed as a tool for the evaluation of the acid resistivity of the experimental leathers as discussed in Section V.

E. TYPICAL MILL OPERATION DATA

Tables 9 and 10 summarize a series of typical mill operation data in the deposition of polymers in the interstices of leathers for the production of acid-resistant experimental items. A number of important physical characteristics are determined at the tannery after the leathers are staked. This is an important step since a side with a rough feel, considerable stiffness and poor gloviness is unsuitable for further work. Tables 11 and 12 summarize the rating of the series of leathers whose mill operation data were summarized in Tables 9 and 10.

TABLE 9

DEPOSITION OF POLYMERS INTO THE INTERSTICES OF LEATHERS BY THE EMULSION METHOD

(Mill Operation Data Series 230-238)

Run No.	Wt. of Dry Leather Grams /a/	Emulsion			Mill Operation /d/		
		Polymer Plasticizer /b/	pH /c/	Solids % /c/	pH of Spent Liquor	Exhaustion % /e/	Depn. % /f/
230	296	Thiokol LP-2 DOP-160	7.5	3	5.9	98	19
231	316	Thiokol DOP-160	7.5	3	3.9	100	10
232	288	Thiokol Kel-F 160	8.1	5	4.7	98	9.8
233	248	Thiokol Kel-F 160	8.1	5	4.6	95	19
234	208	Vistanex MS IP-160	7.9	3	4.4	98	9.7
235	226	Vistanex MS IP-160	7.9	3	3.8	82	17
236	477	Vistanex MS DOP-160	7.4	3	4.0	83	8.7
237	337	Vistanex MS DOP-160	7.4	3	4.2	65	13
238	250	Control Fat-Liquor	7.8	3	4.5	100	20

/a/ Calculated as 40% of the wet leather after passing through wringer; /b/ the abbreviations DOP, IP, etc., refer to plasticizer and the number after it to the emulsifying system as explained in Table8; /c/ pH and solids of diluted emulsion just before mill operation; /d/ mill operation time 60 to 90 minutes; /e/ wt. of solids deposited/wt. of solids in original emulsion places in the mill; /f/ wt. of solids deposited/wt. of dry leather.x 100 = per cent deposition.

TABLE 10

DEPOSITION OF POLYMERS INTO THE INTERSTICES OF LEATHERS BY THE EMULSION METHOD

(Mill Operation Data Series 240-249)

Run No.	Wt. of Dry Leather Grams /a/	Emulsion			Mill Operation /d/		
		Polymer Plasticizer /b/	pH /c/	Solids % /c/	pH of Spent Liquor	Exhaustion % /e/	Depn. % /f/
240	220	Thiokol Polymer B DOP-250	7.4	3	4.6	99	19.8
241	202	Thiokol Polymer B IP-200	7.15	3	4.8	98	19.5
242	180	Thiokol Polymer B DOP-260	5.9	3	5.0	Incomplete - Emulsion broke rapidly /g/	
243	187	Thiokol TCP-160	5.7	3	4.5	100	21
244	266	Thiokol Vistanex DOP-350	6.75	4	4.4	99	19.8
245	318	Thiokol IP-200	7.7	3	4.6	98	19.5
246	316	Thiokol Polymer B DOP-	7.5	4	4.0	87	17.8
247	278	Thiokol Polymer B Vistanex DOP-	7.1	3	5.1	80	22
248	230	Polymer B DOP-	7.3	3	5.6	94	18.7
249	201	Polymer B DOP	7.9	3	5.7	100	20

(Footnotes to Table 10 on following page)

Footnotes. Table 10: /a/ Calculated as 40% of the wet leather after passing through wringer; /b/ the abbreviations DOP, IP, etc., refer to plasticizer and the number after it to the emulsifying system as explained in Table 8; /c/ pH and solids of diluted emulsion just before mill operation; /d/ mill operation time 60 to 90 minutes; /e/ wt. of solids deposited/wt. of solids in original emulsion placed in the mill x 100 = %; /f/ wt. of solids deposited/wt. of dry leather x 100 = %; /g/ emulsion broken within ten minutes, with deposition of the polymer on the sides of the mill and surface of leather. This is due to the cationic emulsifying system; the leather was tumbled for 30 minutes then removed, wiped off and sent to the tannery. A small amount of polymer was deposited as shown by the physical characteristics in Table 11.

TABLE 11

PHYSICAL CHARACTERISTICS OF LEATHERS TREATED WITH POLYMERS

(Series 230-238)

Run No.	Type of Polymer Deposited /a/	Per Cent of Plast. /b/	Level of Depn. % /c/	Physical Characteristics /d/ Gloviness	Appearance	Surface Feel
230	Thiokol-DOP	7	19	C	A	C
231	Thiokol-DOP	7	10	B	A	B
232	Thiokol-Kel-F	30	9.8	B	A	B-plus
233	Thiokol-Kel-F	30	19	A	A	A
234	Vistanex-IP	28	9.7	B	B	A
235	Vistanex-IP	28	17	B-plus	A	C
236	Vistanex-DOP	28	8.7	A	A	C
237	Vistanex-DOP	28	13	B-plus	C	D
238	Control /e/ Fat-Liquor	-	20	A	A	A

/a/ Thiokol refers to Thiokol L-P-2 and Vistanex to Vistanex MS as described in Table 6; /b/ weight of plasticizer/weight of polymer x 100 = %; /c/ same figure as given in the last column of the preceding Table; /d/ ratings as given by the Tannery: A = excellent, B = very good, C = good, D = fair; /e/ fat-liquor consists of a 60-40 mixture of raw and sulfated neatsfoot oils.

TABLE 12

PHYSICAL CHARACTERISTICS OF LEATHERS TREATED WITH POLYMERS
(Series 240-249)

Run No.	Type of Polymer /a/		Plastic. % /b/	Level of /c/ Depn.	Physical Characteristics /d/		
					Gloviness	Appearance	Surface Feel
240	Thiokol Polymer B	DOP	18	19.8	C-plus	C	B
241	Thiokol Polymer B	JP	18	19.5	A	B-plus	A
242	Thiokol Polymer B	DOP	18	/e/	B	A	A
243	Thiokol	TCP	25	21	A	B-plus	A
244	Thiokol Vistanex	DOP	18	19.8	B-plus	B	B
245	Thiokol	IP	25	19.5	A-	A	A
246	Thiokol Polymer B	DOP	43	17.8	A-	A	A
247	Thiokol Polymer B Vistanex	DOP	45	22	A	A	A
248	Polymer B	DOP	20	18.7	A	A	A
249	Polymer B	DOP	20	20	A	A	A

/a/ Thiokol refers to Thiokol L-P-2 and Vistanex to Vistanex MS as described in Table 6; /b/ the figure represents the ratio of plasticizer to polymer x 100 = %; /c/ same figure as given in the last column of the preceding Table; /d/ ratings as given by the Tannery are substantially the same as rated at our laboratory; /e/ not determined.

SECTION V

DEPOSITION OF THE ACID RESISTANT FILMS

A. INTRODUCTION

The leathers with the polymer "filler" do not show any appreciable resistance to fuming nitric acid. Extensive tests using the acid cup test established that an appreciable acid resistance is obtained only by the deposition of a continuous film of a polymer which exhibits chemical inertness. The factors which are of importance in obtaining a surface film with adequate acid-resistance are: (a) composition of the film; (b) method of application; (c) adherence, anchorage and abrasion resistance of the film; (d) thickness and uniformity of the film; (e) flexibility; (f) tackiness.

In order to obtain an adequate description and understanding of these factors it is necessary to describe the methods of evaluation employed for the measurement of resistance to fuming nitric acid, which were the criteria employed to select the film materials and solve most of the problems present in the preceding paragraph.

B. METHODS FOR MEASURING RESISTIVITY TO FUMING NITRIC ACID

1. The Acid Cup Test

The acid cup is made of stainless steel and consists of a lower section on which a circle of about one inch of leather to be tested is fitted in at two short posts. The upper section is then screwed onto the lower one and tightened. Next, about 5 ml of fuming nitric acid is poured into the cup, which is then placed on a tripod with a mirror underneath to show any rapid passage of acid. After 30 minutes from the time the acid was added the acid cup is emptied and washed with water; the sample of leather is then removed from the cup and held under a stream of water to remove as much of the acid as possible. The leather is then neutralized for 30 minutes in a solution of 5% sodium bicarbonate. The sample is washed again, this time being gently rubbed so as to remove portions of loose grain which may have been attacked. Once again the sample is immersed for 30 minutes in a 0.5% solution of ammonium and sodium bicarbonate, washed, rubbed, examined, and placed in tap water for 24 hours. The leather is then dried in the air, after which time it is evaluated on the basis of appearance and amount of deterioration of the grain and flesh due to the action of the nitric acid. Figure 13 on page 44 shows clearly the appearance of a leather sample which has been exposed in the acid cup to fuming nitric acid.

2. Acid Permeability Test

The apparatus employed is shown in Figure 1. The circle of leather (shown in black) between the two arms of the apparatus is 45 mm in diameter and is held tightly by means of two clamps fitting on either side of the semiball joints of the two arms.

The calibration of the apparatus was done in the usual manner. The data obtained were in very close agreement with the values calculated from the activity coefficients. For example the calculated pH for 0.01 molal solution of nitric acid is 2.0448 and the pH value found was 2.08.

The test is made by inserting the leather sample disc between the two arms of the empty apparatus, then pouring into one fuming nitric acid and in the other distilled water as indicated in Figure 1 shown on next page. The apparatus is adjusted and the glass electrode is inserted into the arm containing water and the pH is adjusted by the addition of small droplets of very dilute acid or alkali to 6.0. The readings are taken every 15 minutes, then at whatever intervals the rate of observed change requires, and are continued until a pH of about 2.0 is reached.

In plotting acid permeability data it is convenient to use the interval of time required for the water to reach pH 3.0 or 2.8 which corresponds by the standardization of the apparatus to the passage of 6 grams of nitric acid per square meter of leather. The rate of change from pH 6.0 to about 3.0 is fairly constant, but as is to be expected, the rate of change from pH 3.0 to pH 2.0 varies. In some samples it is rapid, indicating that as soon as some acid penetration has taken place, oxidative decomposition of the fibers begins and rapid failure occurs. In other samples the interval of time required to change the pH from 3 to 2 is two or three times the interval required to change from pH 6 to 3.0.

It was decided early in the work of the project that a desirable goal was to obtain a treated leather which on the permeability test required 8 to 9 hours for a change of pH from 6 to 3.0.

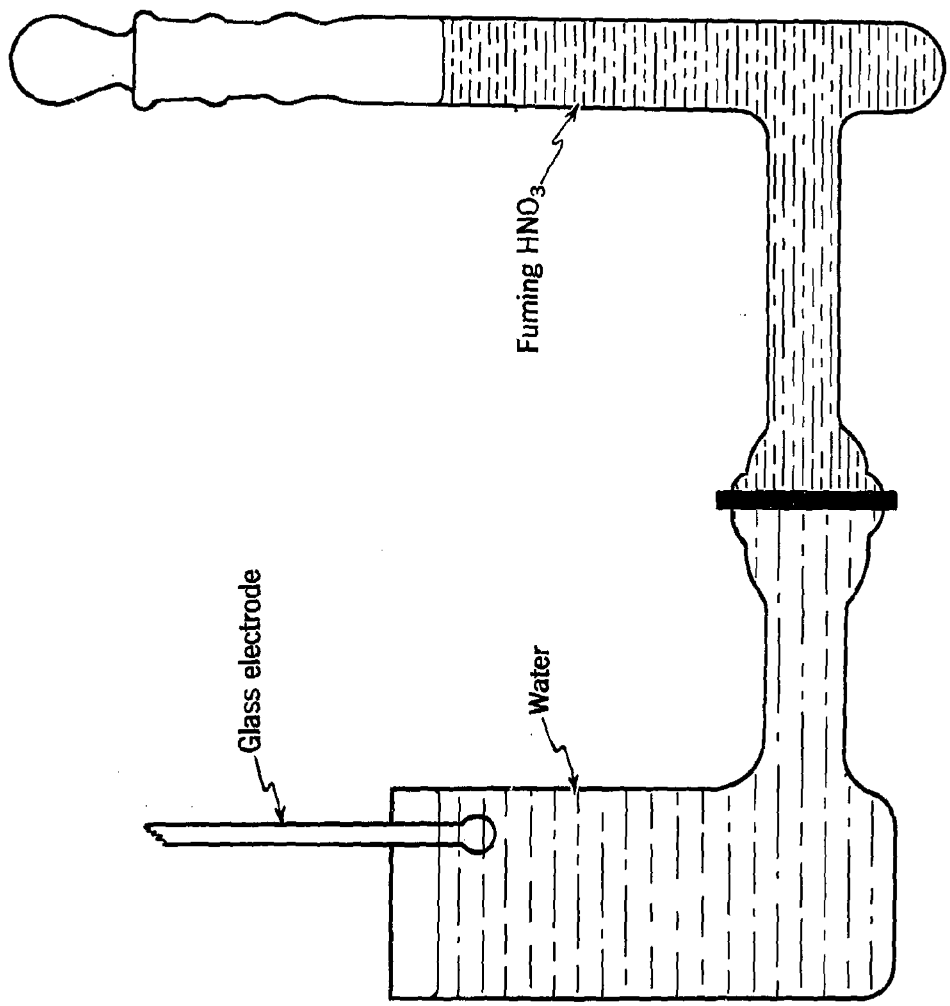


FIGURE 1. Apparatus for Acid-Permeability Test.

Figure 2 shows the appearance of several samples of leather after removal from the permeability apparatus, with subsequent neutralization and drying. Sample No. 2356 shows complete disintegration after 22 hours, while sample No. 2382 was unsuccessful due to excessive pressure by the semiball joints of the apparatus. The other three samples are typical of the appearance of leathers with good protection.

2356
Complete Penetration
at 22 hrs, pH 2.0

2381
Intact But Puckered
With Blisters at 24
hrs, pH 2.2

2382
Failure of Film Due To
Pressure of Semi-Ball
Joints of Apparatus at
20.5 hrs, pH 1.9

2391
Blistered in Few
Places at 20.5 hrs,
pH 1.8

2392
Blistered in Few
Places at 20.5 hrs,
pH 1.9

Appearance of Leather Removed From Permeability
Apparatus After Neutralization

IGURE 2. Photograph showing appearance of various samples of leather after removal from the permeability apparatus and neutralization. Description is given under each sample.

3. Microscopical Test

The steel cup method is a good screening test. The acid permeability test is an excellent method for obtaining information as to the overall performance, but fails to give any information as to the causes of failure of the acid resistant films or structural factors which determine good or poor performance.

The microscopical test is performed on a section of leather which is cut from the sample removed from the acid-permeability cell, as shown on the upper right hand corner of the photograph in Figure 13, page 44. The section is cut in such a manner that it contains an area exposed to fuming nitric acid and an area which is on the outside of the permeability cell. Thus sections can be made from both areas. With patience and care a micro section can be prepared which is at the junction of exposed and unexposed areas. Microphotographs of this type will be found in part D of this Section, in which the microscopical method is employed to correlate data obtained from the acid-cup and acid-permeability tests.

C. COMPOSITION AND METHOD OF APPLICATION OF THE ACID RESISTANT FILM

A variety of film forming materials were tested mostly by application to leathers followed by testing for acid resistivity as outlined in the preceding paragraph. In a few cases films were cast separately and then tested.

Table 13 lists a number of the materials tested for acid resistivity and a qualitative rating of their performance.

The method employed for the deposition of the film in the laboratory scale production was to prepare a 10% solution of the polymer in xylene or a mixture of xylene and toluene and apply the solution in 4 or more coats by brushing. This method involves difficulties in that many of the polymers give very viscous solutions at a 10% concentration. When the solution is diluted to 5% another difficulty is encountered; the solution penetrates within the interstices and fails to form a film. Therefore the first or base coat is applied so as to form an impervious layer; the samples are heated for several hours at 60°C to evaporate the solvent and then a second and third coat, etc. is applied until the film of the desired thickness is built up.

The method for the deposition of the film by brushing has a number of limitations. Aside from the time element, it requires care to obtain a uniform film free from occluded gases (bubbles) or solvent, which become points of weakness in the attack by acid.

The problem of deposition of film in pilot scale production was not solved. Some exploratory work was done at The Greenebaum Tanning Company which indicated that with the proper spray equipment a method could be developed for the deposition of film.

TABLE 13

MATERIALS APPLIED AS FILMS ON LEATHERS AND TESTED FOR RESISTANCE TO FUMING NITRIC ACID

Material	Application	Resistance to Fuming Nitric Acid of Film 5 to 6 ml Thickness
G. E. silicone /a/	As a film	Fair
Methyl silicone /b/	"	"
Ethyl silicone /c/	"	"
Ethyl aminosilane /c/	"	"
Phenyl aminosilane /c/	"	"
Butyl rubber /d/	"	Good
Neoprene rubber /d/	"	Poor
Molybdenum sulfide	As a filler	"
Zinc silicate	"	"
Zirconium silicate	"	"
Zinc oxide	"	Fair
Alathon-1 /e/	As a film	"
Alathon-7 /e/	"	Good
Alathon-8 /e/	"	"
Vistanex-MS /f/	"	Fair
Vistanex-B80 /f/	"	Very good
Thiokol LP-2 /g/	"	Fair
Kel-F Polymer 300 /h/	"	Good

/a/ General Electric Co.; /b/ Dow Corning Corp.; /c/ Prepared at The Synthetical Laboratories; /d/ W. H. Salisbury & Co.; /e/ E. I. DuPont deNemours; /f/ Enjay Corp.; /g/ Thiokol Chemical Corp.; /h/ M. W. Kellogg Co.

In a related project (Connecticut Hard Rubber Co.) the same type of polymer* was applied on glass cloth by calendering at temperatures of 350 to 400°F. Though it is generally known that leather deteriorates rapidly at temperatures above 100°C (212°F) the heat stability of leathers (for short periods of time) was investigated. It was established that exposing leathers to temperatures above 300°F for 2 to 3 minutes produces drastic alterations with considerable shrinkage. The changes are small if the leathers are exposed for 2 to 3 minutes at temperatures below 300°F.

D. ADHERENCE AND UNIFORMITY OF THE FILM

1. Anchorage of Film

Two important factors in the performance of the film are the adherence and uniformity of the film. The abrasion resistance depends to a large extent on these two factors. If a film does not form a very tight bond with the surface of the leather it has poor abrasion resistance, peels off readily and shows poor acid-resistance.

For proper anchorage there must be first deposited within the interstices of leather a "filler polymer" as described in Section IV. For example, if the film to be deposited consists of Kel-F elastomer (Kel-F X-300) excellent anchorage and adherence is obtained by depositing first within the interstices Kel-F NW-25 plasticized with Kel-F Oil #10.

2. Uniformity of Film

Aside from variation in thickness of the film occluded gases and solvent produce pitting or pin holes which become points of attack when the leather is exposed to the acid. In very thin films the lack of uniformity is more critical than in films above 5 to 6 mils thickness.

The uniformity of the film depends on several different factors. The variation in density over different areas of the hide (back, breast, belly, shank) is one contributing factor; low fiber density or loose areas lead to more absorption of the solution and hence non-uniform film. Other factors are the viscosity of the polymer solution and the technique of application. Careless and hurried application leads to a large number of occluded air bubbles which later give rise to either pin holes or pits. Similarly, application of thick coats will tend to occlude solvent giving rise to areas with weak acid-resistance.

3. Microscopical Evidence on the Importance of Adherence and Uniformity

The microphotographs of experimental sections of leathers shown in Figures 3, 4, 5 and 6 illustrate the method of deposition of the acid resistant film consisting of Vistanex B-80. Figure 3, as the caption indicates, shows a microsection of the grain area of cowside leather after deposition of the "filler polymer" within the interstices and slight buffing to effect a good bond.

* (Vistanex B-80)

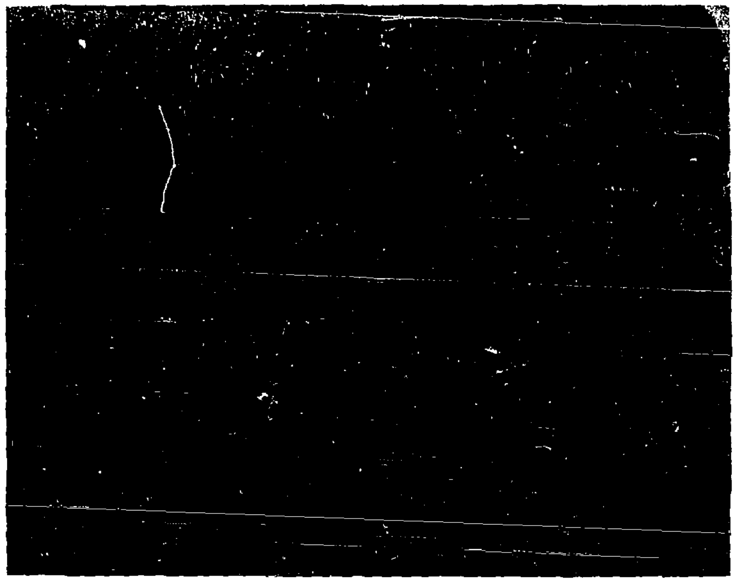


FIGURE 3. Microsection grain area of cowside leather after deposition of polymer and slight buffing to effect a good bond with the acid-resistant film. **(Sample No. 234)**

Figures 4 and 5 represent two successive applications of the film forming polymer.

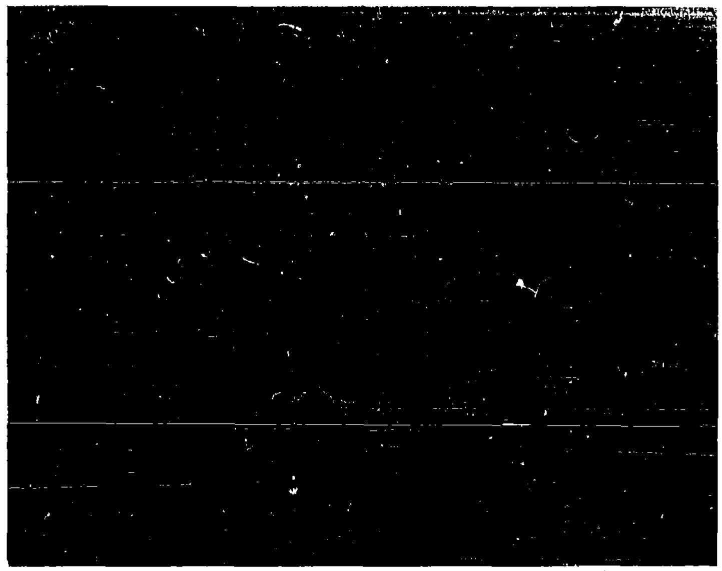


FIGURE 4. Section of leather with the first coat of the acid resistant film. Thickness 2.3 mils.

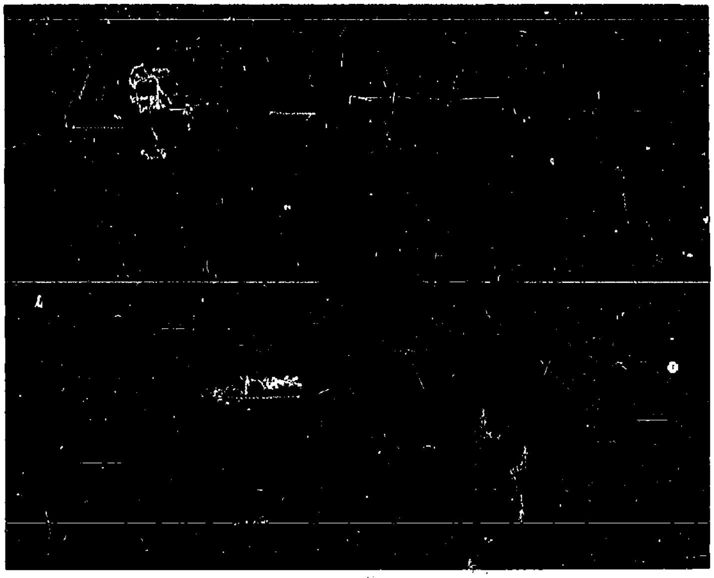


FIGURE 5. Section of leather with film of 3 to 4 mils thickness. Close-up of hair follicles of grain area to show penetration of polymer and bond of the acid-resistant film.

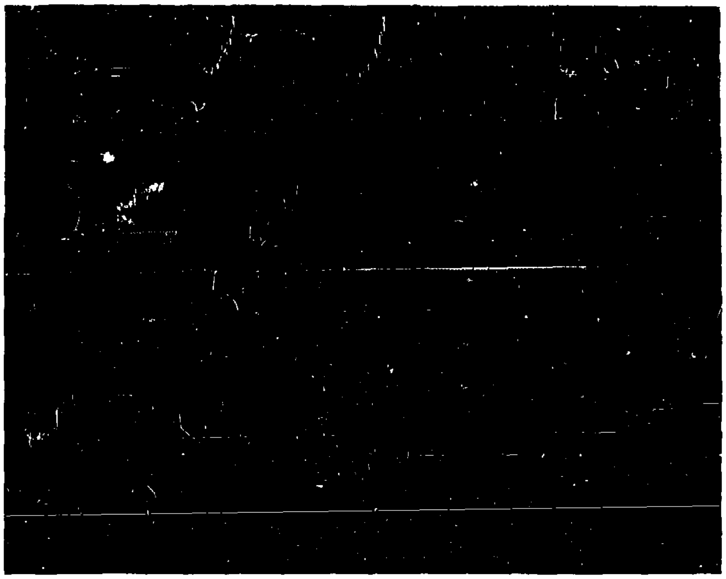


FIGURE 6. Desired thickness of film for maximum acid resistance 5 to 6 mils.

Poor anchorage and adherence is shown by the microphotographs of Figures 7, 8 and 9. In Figure 7 the film having poor adherence is arched by the action of the acid.

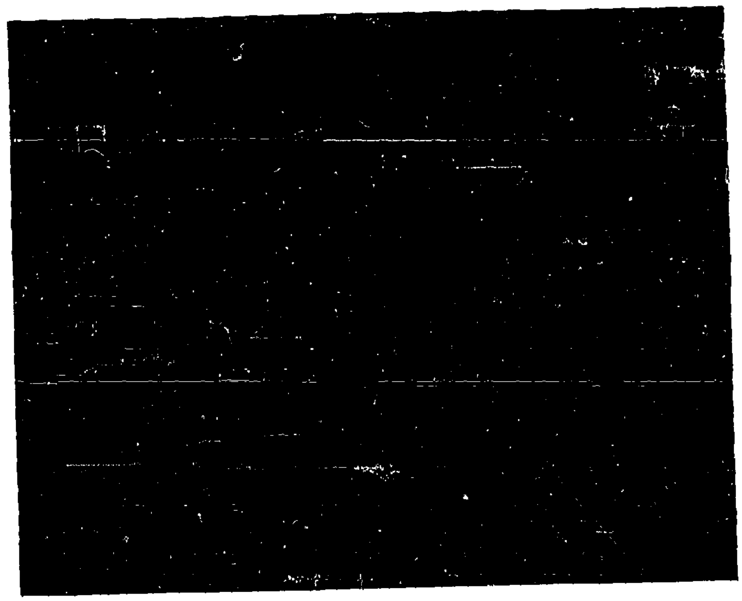


FIGURE 7. Sample 244 A-2. Section taken from blistered area exposed to nitric acid. Note that the bond between film and leather surface is poor and that the film has arched, although no break occurred. Grain has been attacked.

Figures 8 and 9 are from adjacent areas of the same sample. The film has been ruptured and erosion has begun.

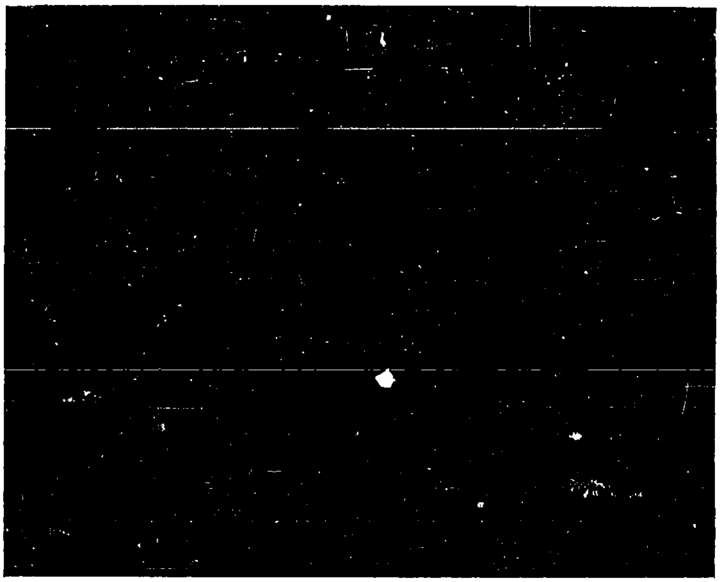


FIGURE 8. Sample 244 A-3. Break of the film and also beginning of erosion of the fibers.

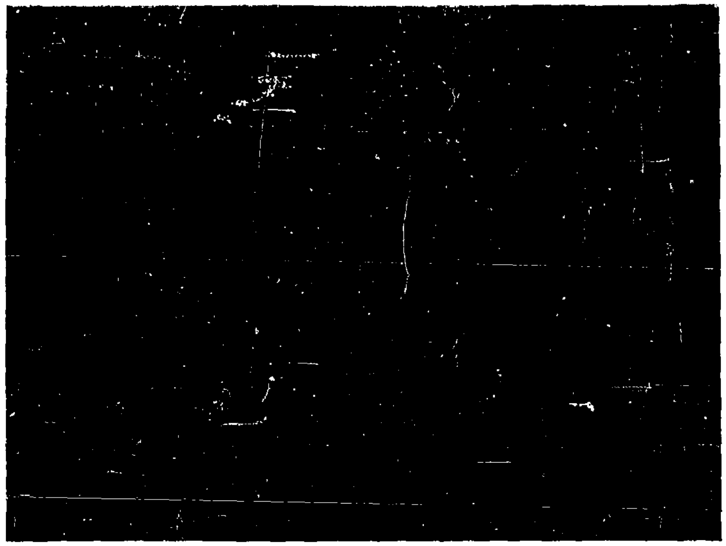


FIGURE 9. Sample 235 A. Break of the acid resistant film. The naked eye fails to reveal any rupture. Note the curled and shriveled appearance of the film and the darkened areas at the left. These represent changes by the action of acid mainly tanning which eventually lead to stiffness and hardness.

The effect of nonuniformity is illustrated in Figures 10 and 11. Though the adherence of the film is good and no break has occurred the pin hole which appears on the upper right hand corner of Figure 10 shows alteration of the fiber structure of the leather as black areas. The thickness of this particular film was 2 to 3 mils and the pit or pin hole became the point of weakness leading to low resistance.

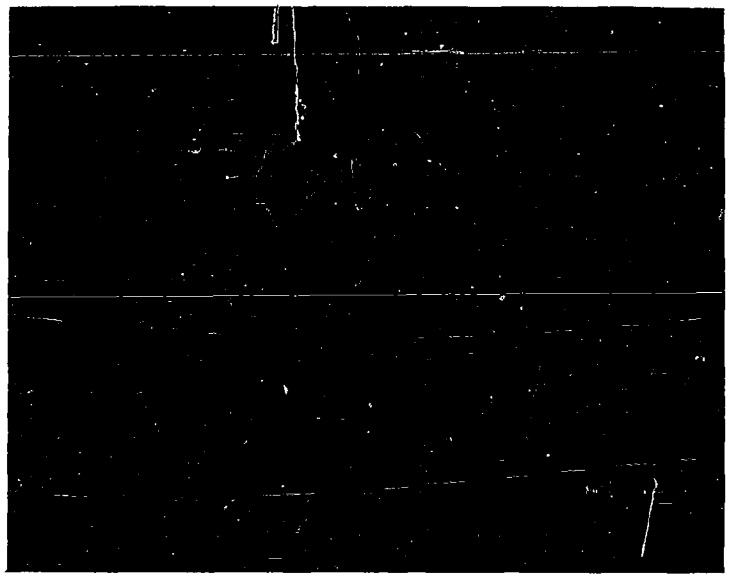


FIGURE 10. Sample 235-B. An excellent example of the boundary of exposed and unexposed areas of leather to nitric acid. The area to the right is unexposed. Note that the film at the upper right begins to thicken and the fibers show no darkened areas. At the left the film has not been broken but has been shriveled and some corrosion and permeation has produced darkened areas (See No. 11 for close-up of the darkened areas.)

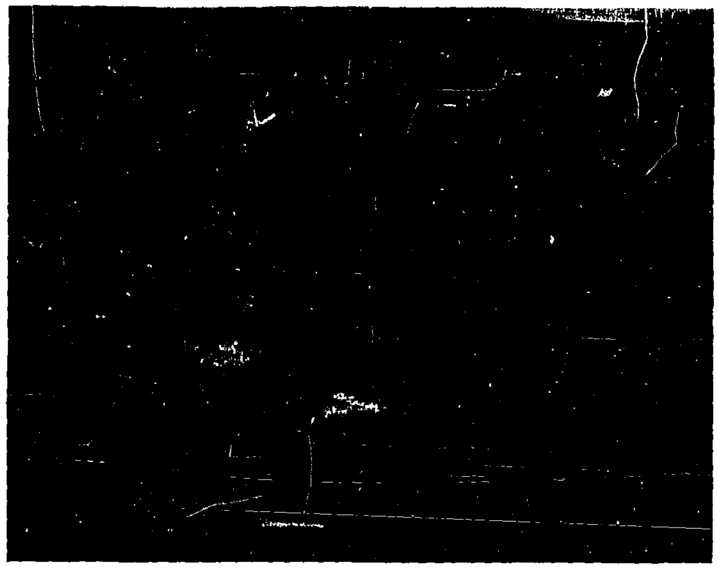


FIGURE 11. Close-up of the darkened areas shown in the section No. 10. The "pin-hole" in the film from which the acid probably permeated is the dark-eroded spot on the upper middle. Below it and within the fiber bundles black spots indicate changes in the interstices of leather by the acid. Note that the black spots diminish toward the flesh side (lower). Note that the polymer is well distributed but less in the middle. Sections Nos. 10 and 11 show how the microscopical method may be used to detect changes in the internal structure of leather as a result of permeability of acid even when visual examination shows good acid-resistance.

E. THICKNESS OF THE FILM

The importance of the uniformity and thickness of the films became apparent by the wide variations in the performance of leathers treated with the same type of polymeric film. Table 14 gives a summary of typical data of leathers having the same film composition but exhibiting wide variations in acid resistance. The same data are summarized graphically in Figure 12.

In order to establish the effect of the thickness of the film, a series of experimental leathers were prepared using the same polymer. The leathers were treated with three coats of the polymer solution. After each coating the samples were heated for 24 to 28 hours at 60°C to insure removal of all solvent and a small section was cut for microscopical examination. Tables 15 and 16, and Figures 13 and 14 summarize the performance data of one series. Inspection of the data (particularly the microscopical examination in Table 16) shows that the thickness of the film plus uniformity and anchorage determine its acid resistivity. This study pointed out the way for the deposition of films having resistance of 100 to 150 hours described in Section VI.

TABLE 14

SUMMARY OF DATA ON EXPERIMENTAL LEATHERS WHICH HAVE SOME SURFACE FILM COMPOSITION

Sample No.	Polymers Interstices and % Depn.	Polymers in Film	Thickness of Film (mils)	Time for Change of pH from 6 to 2.2	Appearance of Leather after removal from test cell and neutralization
230-1	Thiokol DOP-19%	Vistanex B-80	1.4	20	Film peels off -- otherwise not attacked
231-2	Thiokol DOP-10%	Vistanex B-80 Butyl rubber	1.5	14	Complete penetration leather attacked
234-1	Vistanex MS-IP-9.7%	Vistanex 80 Alathon 20	1.6	5	Complete penetration
235-1	Vistanex MS-IP-17%	Vistanex B-80	1.8	21.5	Intact -- few small blisters. No tanning
235-2	Vistanex MS-IP-17%	Vistanex B-80	2.7	46	Excellent -- one small blister. No tanning or drying
235-3	Vistanex MS-IP-17%	Vistanex B-80	1.4	14	Leather badly attacked and tanned
235-B-1	Vistanex MS-IP-17%	Vistanex Alathon	1.5	5.25	Leather penetrated and tanned
236-1	Vistanex MS-DOP-8.7%	Vistanex	2.2	5	Large hole and small blisters. Leather attacked.
236-2	Vistanex MS-DOP-8.7%	Vistanex	2.3	5	Numerous blisters. Leather attacked.
244-2	Thiokol Vistanex MS-19.8%	Vistanex	2.3	25	No visible damage.

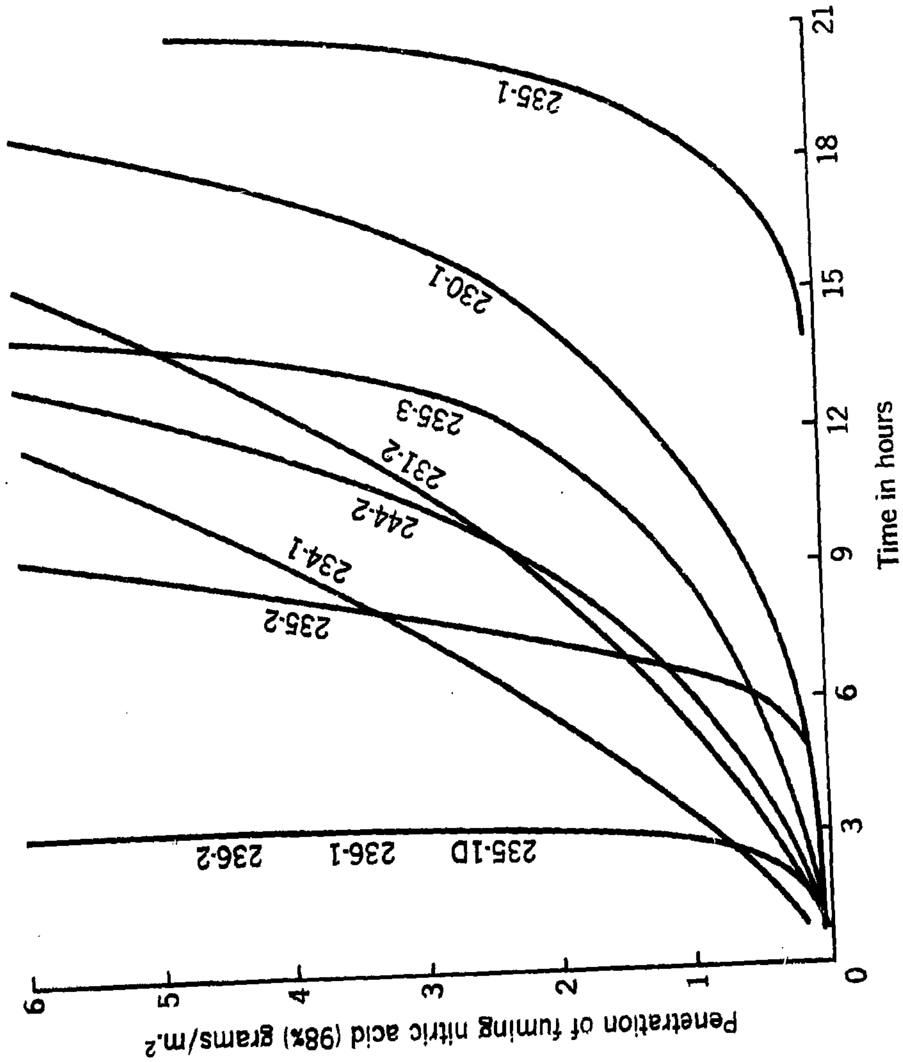


FIGURE 12. Graphical summary of acid permeability data of experimental leathers listed in Table 14.

TABLE 15

SUMMARY OF DATA ON SERIES OF EXPERIMENTAL LEATHERS TO DETERMINE RELATION BETWEEN ACID RESISTIVITY, THICKNESS AND OTHER PROPERTIES OF THE FILM

Leather Number	Total Thickness of film in mils /b/			Evaluation after 3rd coat	
	1st coat	2nd coat	3rd coat	Steel Cup Test /c/	Permeability Hours /d/
234 (XYZ) /a/	1	3	5.5-6	Excellent appearance no stiffness on standing	130
235 (XYZ)	1	3	6-6.5	Excellent appearance; no stiffness on standing	103 63
247 (XYZ)	1	4	6.5-7	Excellent appearance; develop slight stiffness on standing	59 59

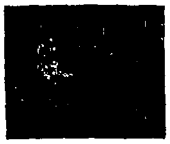
/a/ The numbers 234, 235, 247 refer to the emulsion treated leathers on which film was deposited; X stands for the sample after the first coat, Y for the sample after the second, and Z for the final sample which was evaluated; /b/ accurate measurements over several microsections by micrometer scale within the eyepiece; maximum variability over entire section 0.2 to 0.5 mils; /c/ duplicate tests of exposure to fuming nitric acid for 0.5 hours; /d/ duplicate tests in permeability cell indicating the number of hours required for water part of the cell to change from pH 6 to pH 2.0. The duplicate of 234-Z broke at the edge (from pressure of the clamp) at 35 hours. For further correlation see Figures 12, 13 and 14, and Table 16.

TABLE 16

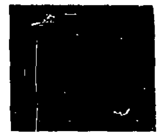
SUMMARY OF DATA ON MICROSCOPICAL EXAMINATION, ABRASION RESISTANCE AND FLEXIBILITY OF SAMPLES OF EXPERIMENTAL LEATHERS ON WHICH ACCURATE DEPOSITION OF ACID-RESISTANT FILM WAS MADE

Sample Number /a/	Abrasion Resistance /b/	Flexibility /c/	Microscopical Examination: Before Acid Exposure /d/	Microscopical Examination: After Acid Exposure /e/
234-Z (series)	Good--film piles up but does not peel	Medium flexibility	Film adheres uniformly to grain and is anchored deep within hair follicles; no bubbles at grain and film interface.	Shrinkage of film and some slight changes within the fiber bundles; no film rupture.
235-Z (series)	Same as above	Least flexible	Film uniform but not as well anchored as 234-Z; occasional bubble at boundary of film and grain.	Shrinkage of film, more extensive in pits, a few ruptures of film and slight corrosion of fiber bundles.
247-Z (series)	Fair; peels readily when scratched repeatedly	Most flexible	Film less uniform than 234-Z and 235-Z series; numerous bubbles at boundary of film and grain.	Film ruptured in many areas; more extensive alteration of fiber bundles.

/a/ See Table 15; /b/ sharp instrument drawn across the leather and also leather bent and rubbed against abrasive surface; /c/leather bent and allowed to regain its former position; /d/ sections from the entire series were examined , as well as sections from the unexposed areas of the samples used for the permeability and acid cup tests; /f/ sections from the areas exposed to the acid in the steel cup test and permeability cell. Several sections were made, particularly in the areas where tiny blisters were seen through a magnifying glass.



Thickness of Acid Resistant Film 5.5 MILS

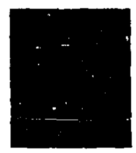


2 3 4

Sample of Treated Leather After Acid Cup Tests 0.5 HRS

After 130 HRS in Acid Permeability Apparatus (see microscopical section)

Thickness of Acid Resistant Film 6.4 MILS



235 Z-1

Sample of Treated Leather After Acid Cup Tests 0.5 HRS

After 103 HRS in Acid Permeability Apparatus

Thickness of Acid Resistant Film 6.9 MILS

247 Z-1

Sample of Treated Leather After Acid Cup Tests 0.5 HRS

After 59 HRS in Acid Permeability Apparatus

FIGURE 13. Photographs of several pieces of experimental leathers having the same type of acid resistant film, before and after acid cup test and acid permeability test.

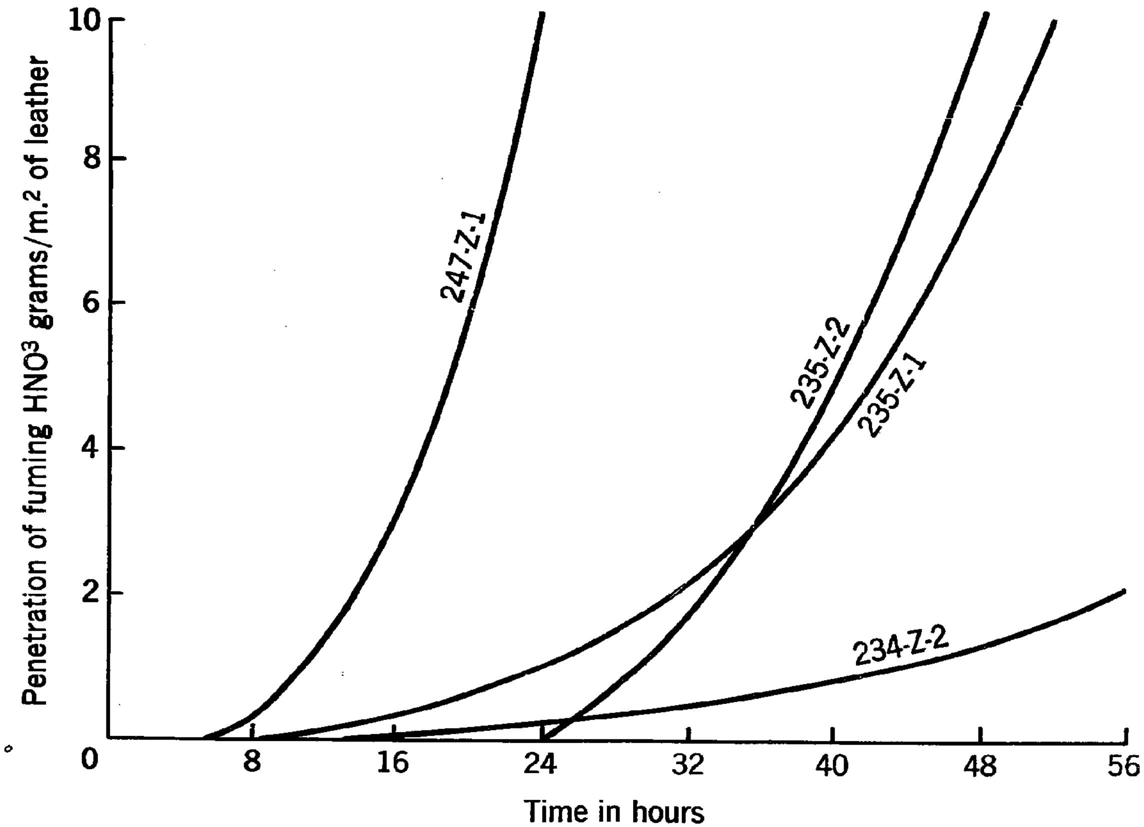


FIGURE 14. Graphical representation of acid-permeability of experimental leathers summarized in Tables 15 and 16.

F. FLEXIBILITY AND TACKINESS OF THE FILMS

The flexibility of films of approximately the same thickness depends almost entirely on the nature of the polymer. Though there is a variation in flexibility between various polymeric films this was not found to be critical. In upper leathers a great deal of flexibility is not desirable. However, in glove leathers flexibility is of importance. It was found that starting with 2.5 to 3-ounce leather the addition of a film 5 to 6 mils in thickness reduces the flexibility. However, if a 2-ounce leather is employed the resulting leather is very flexible.

The problem of tackiness is one which was not completely solved. Most of the films which exhibit the best acid resistance also show tackiness. Of those which show good acid resistance only one, Kel-F Elastomer X-300 exhibits no tackiness when deposited as a film. However, this polymer is available only in experimental quantities and is twenty times as expensive as the other polymers.

Only a small amount of work was devoted toward the solution of this problem. Treatment with a solution of sulfur monochloride and irradiation with ultra violet rays reduces the tackiness. Application of talc or soapstone removes the residual tackiness which reappears when all talc is removed, but to a smaller degree.

SECTION VI

LABORATORY PRODUCTION OF LEATHERS RESISTANT TO FUMING NITRIC ACID (97% min) AND HYDROGEN PEROXIDE (90%)

A. LEATHERS

For glove leathers either cowsides or horsesides of 2-ounce thickness full grain, chrometanned according to standard procedures are employed.

For upper leathers steerhide of 4-ounce thickness and chrometanned (but not retanned with vegetable) is used.

The use of splits was tried in collaboration with Mr. Robert Lichtman of Lichtman Tanning Corporation in Newark, New Jersey. It appears that the use of splits for uppers is feasible since a film 8 to 10 mils in thickness can be deposited, and the leather is not extensively flexed ana distorted.

Leathers tanned with Politan tannage can be successfully employed in the production of acid-resistant leathers.

B. POLYMERS

Of the polymers tried only two are recommended for the composition of the acid-resistant film. These are: (a) Vistanex B-80 (Enjay Corporation) and (b) Kel-F X-300 plasticized with Kel-F resin X-200 (M. W. Kellogg Co.)

The use of Alathon-1 resin and Alathon-8 in conjunction with Vistanex films was found to lower the acid-resistance and adherence of the film. The tests were extensive and were repeated many times in view of the report from another project that a composition of 80% Vistanex polymer and 20% Alathon-1 resin gave the best results in their tests. The use of Alathon resins together with Vistanex elastomers does not result in homogeneous dispersions. The Alathon resins tend to form "flocks" which when deposited as a film become points of weakness.

The Kel-F elastomer X-300 plasticized with Kel-F resin X-200 offers good acid-resistance, adherence and no tackiness. However, aside from the price factor these materials could be obtained only in small experimental quantities at the time the work was in progress and hence were not tested as extensively as the other films.

Butyl rubber in conjunction with Vistanex elastomers gives rise to the same difficulties as the Alathon resins.

The polymers to be deposited within the interstices of the leathers are (a) for a Vistanex film a Vistanex-MS polymer and Thiokol LP-2 polymer mixture; (b) for the Kel-F elastomer film a Kel-F NW-25 polymer plasticized with Kel-F Oil No. 10.

C. DEPOSITION OF POLYMERS

1. Deposition within the Interstices

The leathers are tanned and preconditioned as described in Section IV. They are then treated for deposition of 10 to 12% of polymer within the interstices. The composition of the emulsion if the surface film is Vistanex is given by Formula A; if the film to be deposited is Kel-F elastomer X-300, the composition of the emulsion is given by Formula B:

	Formula A Grams	Formula B Grams
Thiokol LP-2	87.5	---
Vistanex MS 10%	158.5	---
Kel-F No. 10	---	60
Kel-F NW-25	---	230
Indopols	54.0	---
Xylene	1 070.0	170
Toluene	356.5	100
Emulsifier	21.0	20
Tergitol Masking Odor	2.0	20
Water	1 250.0	2360
Solids per cent	10.0	6.8

The following gives an example of the treatment. A section of cowside leather weighing 600 grams (dry weight) previously preconditioned and thoroughly rewetted was tumbled in the mill with water at 50 to 60°C. The water was drained and 720 grams of Emulsion A previously heated to 60°C was diluted in the mill with hot water so that the emulsion contained 3% solids. The purpose in using 720 grams was to deposit within the interstices of the leather approximately 12% polymer. The mill was allowed to run 80 minutes. then 1 ml. of formic acid was added to insure complete exhaustion of the emulsion. After 10 minutes of additional tumbling the spent liquor was withdrawn, the pH and percent solids were determined according to the description given in Section IV.

The initial pH of emulsion A was 8.0, the final pH was 4.5. The spent liquor was collected and analyzed for solids; the amount found was about 2 grams, indicating a substantially complete exhaustion (98%).

2. Deposition of the Acid-Resistant Film

A section measuring approximately 5" x 7" was cut from a sample of cowside which had been treated by the emulsion method so as to deposit in the interstices Vistanex-Thiokol polymer. A diluted (4%) solution of Vistanex B-80 was applied by means of a fine paint brush to the surface of the leather. Since the initial coating serves as the binder between the leather fibers and the acid resistant film it is important that the solution be thick enough to coat the individual fibers and yet thin enough to penetrate the interstices of the grain. The leather was placed in the oven at 60°C and thoroughly dried; then a second coat of a more concentrated solution (10%) of polymer was applied. With the addition of the second coating a thickness of about 3 to 4 mils was obtained. A third and final coat was brushed on after the evaporation of solvent and this too was allowed to dry. Three coats of polymer applied to the surface of a small piece of leather such as this will give a final film thickness of from 5 to 6 mil, provided the polymer added as a film comprises 10 to 12% of the weight of the dry leather. Such a film will withstand the action of fuming nitric acid for over 20 hours. If the film is uniform the resistivity may be as high as 130 to 150 hours.

In order to reduce the tackiness of the surface film it was painted with a 10% solution of sulfur monochloride in carbon tetrachloride and then exposed to ultra violet rays from a mercury vapor lamp at a distance of 18 to 20 inches for 15 minutes. This removes most of the tackiness; any residue is then removed by rubbing into the film talc.

D. TYPICAL PERFORMANCE DATA

Table 17 summarizes typical performance data from a series of experimental leathers produced in the laboratory in order to determine the maximum acid resistivity that can be attained by increasing the film thickness and using methods described.

Figures 15 and 16 summarize graphically the acid permeability data given in Table 17. Figure 15 summarizes the data of experimental leathers which did not show desired acid resistance while Figure 16 shows experimental leathers with excellent acid resistance. The resistivity of the film is shown in Figure 17 representing a microphotograph from a sample exposed to fuming nitric acid in the permeability cell for 130 hours. The micro section was taken from the boundary of exposed and unexposed sections. The film has been compressed by the ball-joints of the apparatus and also by the action of the acid and in spits of these factors it has remained unbroken.

TABLE 17

PERFORMANCE DATA OF EXPERIMENTAL LEATHERS PRODUCED UNDER LABORATORY CONDITIONS FOR RESISTIVITY TO FUMING NITRIC ACID AND 90% HYDROGEN PEROXIDE

No. of Final Sample /a/	Film Polymer	Film Thickness in mils	Acid resistivity: Permeability cell - time in hrs. for change pH 6.0 to pH			Acid resistivity: Steel cup test 0.5 hrs. exposure in fuming HNO_3
267-1 BK	Vistanex (80)	6.7	72 hrs. Exposed area blistered	to	2.2	No damage Slight stiffness
267-2 BY	Vistanex (80)	6.0	48 hrs. Numerous blisters	to	2.2	No damage Slight stiffness
268-1 BK	Vistanex (80)	8.7	95 hrs.	to	3.0	No damage - very slight stiffness
268-2 BY	Vistanex (80)	9.6	123 hrs.	to	2.0	No damage
270-A1 BK	Vistanex (80)	8.7	8[illegible] hrs.	to	3.0	Excellent No stiffness
270-A2 BK	Vistanex (80)	10.2	179 hrs.	to	3.0	Excellent no stiffness
270-B1 BK	Vistanex (80) (80%) Alathon (8) (20%)	5.9	136 hrs.			No damage - very slight stiffness
270-B2 BY	(same as above)	8.7	60 hrs.	to	2.3	No damage - very slight stiffness
269-A1 BK	Kel-F-X-300	2.3	31 hrs.	to	2.0	Excellent; no damage
269-A2 BY	Kel-F-X-300	2.9	27 hrs.	to	2.0	Excellent; no damage
285-1 BK	Vistanex (80)	4	Exposure to 90% hydrogen peroxide (steel cup for 30 minutes)			Excellent; no damage
270-A1 BK	Vistanex (80)	8.7	Exposure to 90% hydrogen peroxide (steel cup for 30 minutes)			Excellent; no damage

/a/ The number refers to the cowside and area; BK - Back, and BY - Belly. The emulsion treatment is shown in Table 5.

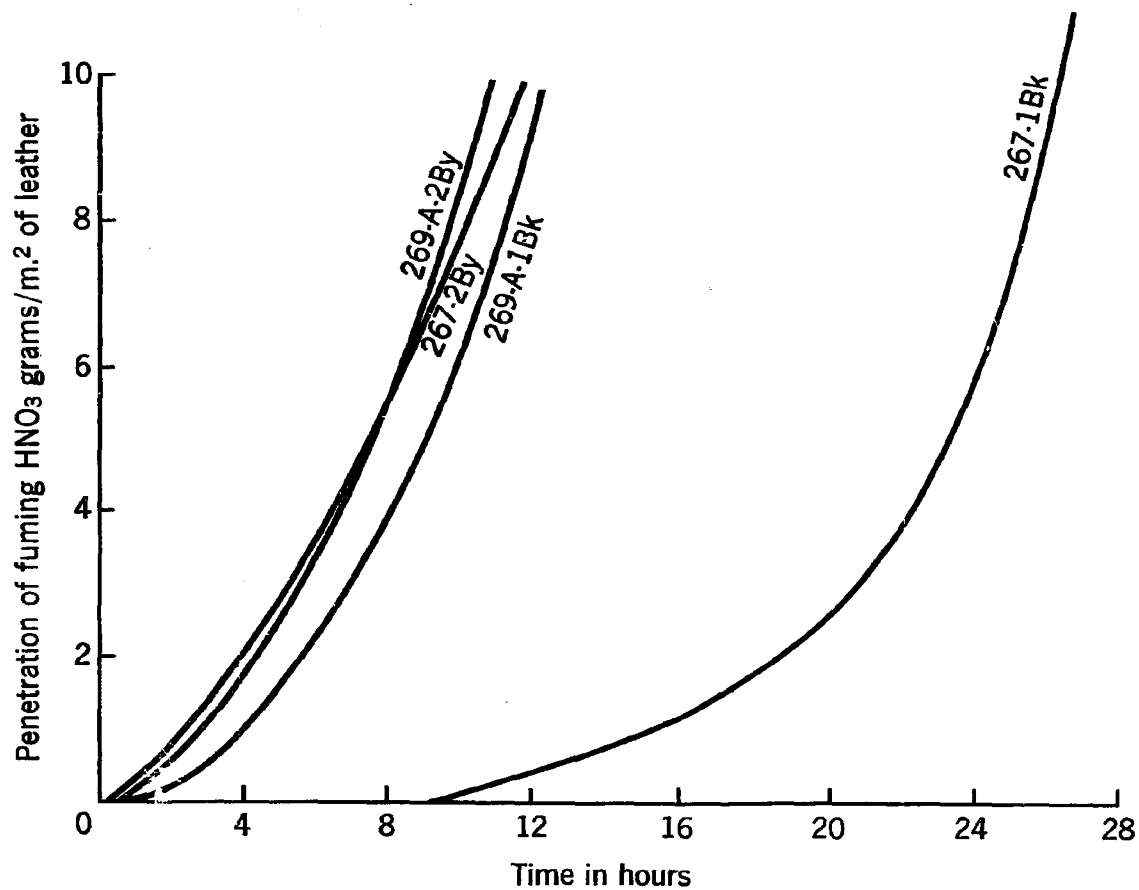


FIGURE 15. Graphical representation of acid-permeabilities of experimental leathers of low resistance.

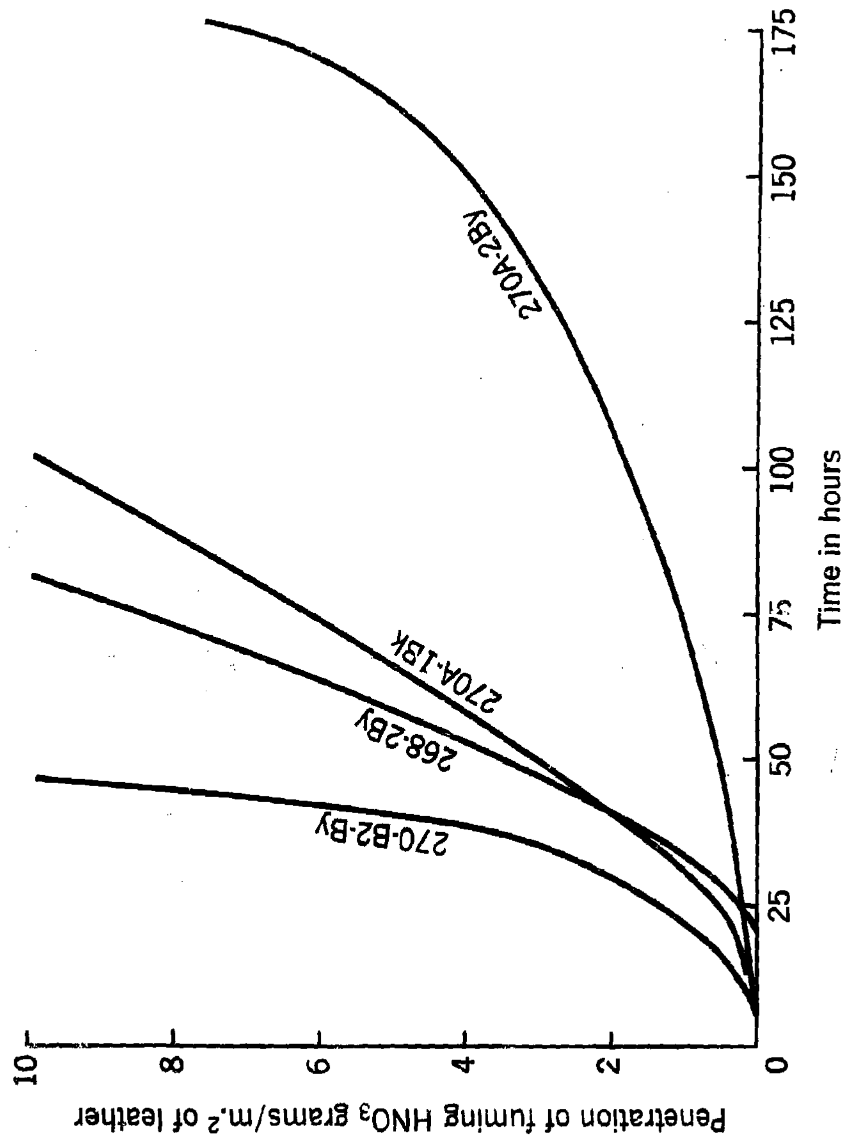


FIGURE 16. Graphical representation of acid-permeabilities of leathers of high acid resistance.

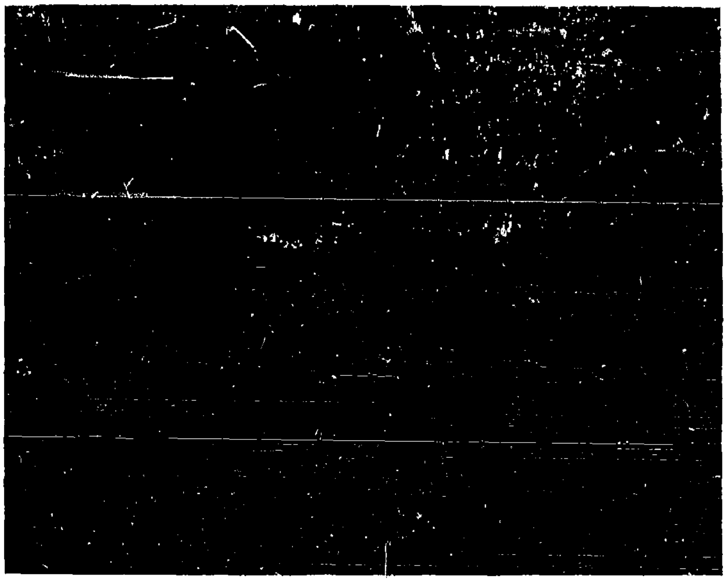


FIGURE 17. A good microscopical proof of acid-resistance of treated leather. The microphotograph represents the boundary of the exposed and unexposed areas after the sample was in the permeability cell for 130 hours. Note that the film though compressed by the apparatus to one-fifth of its former thickness is still intact and that the changes in the interstices are not extensive.

SECTION VII

PILOT SCALE PRODUCTION OF ACID RESISTANT GLOVE LEATHERS

A. INTRODUCTION

The contract provides that "100 square feet of leather shall be submitted which shall be designated by this Center and which has been developed during the course of this contract." However, the contract expired before the laboratory work could be translated to pilot scale production. Therefore the deposition of film on the 100 square feet of leather was produced in accordance with the laboratory method.

Seven cowsides of 2-ounce thickness, weighing 5,550 grams after chrometanning were dyed according to standard tannery procedure and treated for 10% deposition of polymer using the Formula A appearing in Section IV of this report. After the leather was dried, cured and staked it was found by microscopical examination to have a fairly uniform deposition. It was then calendered and buffed and was made ready for the first application by brush of Vistanex B-80 solution. A 10% solution of the polymer in xylene-toluene was diluted with Naphtha (VM&P) to 4%. The first coat was applied so as to obtain an addition of 1 to 2% polymer (based on dry weight). When the solvent had evaporated and the surface of the leather was dry, seven successive coatings were applied, using a solution of 6% solids. While it was possible to obtain a film 7 mil in thickness in the laboratory by 3 to 4 coatings, many difficulties in drying procedures were encountered at the tannery, necessitating more applications than were at first anticipated. After each coating the cowside was hung horizontally in a drying chamber and exposed to circulating warm air at about 60°C. The drying period between coats was about one hour. Great care had to be exercised in applying the Vistanex since it has no flow characteristics and if an excess was used on the 4" brush many bubbles and an uneven surface resulted.

Based on dry weight the film gave an additional weight of about 20% to the leather, and a thickness of 5 to 6 mils.

The final treatment of the leather for removal of tackiness was not very successful. A 10% solution of sulfur monochloride in carbon tetrachloride was sprayed on the film and rapidly dried by cold air. After that the film was exposed for 10 minutes in sections to ultra violet and infra red radiation. The fact that tackiness was completely removed in some sections and only partly so in others indicates both the effectiveness of this procedure and the need for further study. Finally, talc was liberally dusted over the entire surface, carefully wiped with a damp cloth and applied once again, this time very lightly. The finished acid-resistant leather has been rated by the tannery as excellent with respect to gloviness and flexibility. The adherence is very good. The acid resistivity as measured by the permeability cell varies from 50 to 60 hours.